PB81-163305

Effect of Scrubbing Operating Conditions on Adipic Acid Degradation

Acurex Corp.
Morrisville, NC

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Feb 81

U.S. Department of Commerce
National Technical Information Service
NTIS.

PB81-163205

EPA-600/7-81-017
February 1981

Acurex Project 7574

EFFECT OF SCRUBBING OPERATING CONDITIONS ON ADIPIC ACID DEGRADATION

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15 October 1980

Acurex Final Report FR-80-17/SR

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Contract 68-02-3176
Task 4

REPRODUCED BY
NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

IERL-RTP-1136

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-81-017	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Effect of Scrubbing Operating Conditions on Adipic Acid Degradation	5. REPORT DATE FEBRUARY 1981 ISSUING DATE.
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) John C.S. Chang	8. PERFORMING ORGANIZATION REPORT NO. FR-80-17/SR
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation Southeast Regional Office, Route 1 Morrisville, North Carolina 27560	10. PROGRAM ELEMENT NO. EHE625 11. CONTRACT/GRANT NO. 68-02-3176, Task 4
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Task Final; 2-8/80 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Robert H. Borgwardt, Mail Drop 65, 919/541-2336.

16. ABSTRACT The report gives results of adipic acid degradation tests at EPA's IERL-RTP limestone SO2 scrubber, to investigate the effects of operating variables on unaccountable adipic acid loss. It was found that: (1) adipic acid degradation could not be totally quenched by only lowering the pH below 5.0; (2) pH change did significantly affect unaccountable adipic acid loss (other factors may increase the adipic acid degradation rate at both high and low pH); (3) an appreciable amount of adipic acid loss was caused by coprecipitation with calcium sulfite; and (4) forced oxidation could aggravate the adipic acid degradation loss even at pH below 5.0. Adipic acid loss could be reduced: at high sulfite concentrations (the adipic acid degradation rate could be decreased by lowering the destructive free radical concentrations by high total sulfite); in the presence of manganous ion at low pH (the metal ion might act as an inhibitor to the oxidative degradation reaction at low pH); and with high natural oxidation (the adipic acid coprecipitation loss might be reduced with the high natural oxidation). Adipic acid degradation (loss) data were compared from four different test facilities. Most of the data also support these conclusions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Adipic Acid Degradation Sulfur Dioxide Scrubbers Limestone pH Oxidation Sulfites Calcium	Pollution Control Stationary Sources Forced Oxidation Calcium Sulfite	13B 07D 07C 14G 07B 07A,13I 08G

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 29
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

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SUMMARY

A series of adipic acid degradation tests have been conducted at the EPA-IERL-RTP limestone SO_2 Scrubber to investigate the effects of operating variables on unaccountable adipic acid loss. It was found that:

- o adipic acid degradation could not be totally quenched by only lowering the pH values below 5.0
- o pH change did not have a significant effect on unaccountable adipic acid loss. There might be some other factors which could increase the adipic acid degradation rate at both high and low pH values
- o an appreciable amount of adipic acid loss was caused by coprecipitation with calcium sulfite
- o forced oxidation could aggravate the adipic acid degradation loss even at pH below 5.0

The adipic acid loss could be reduced under the following conditions:

- o high sulfite concentration - the adipic acid degradation rate could be decreased by lowering the destructive free radical concentrations by high total sulfite
- o in the presence of manganous ion at low pH - the metal ion might act as an inhibitor to the oxidative degradation reaction at low pH
- o high natural oxidation - the adipic acid coprecipitation loss might be reduced with the high natural oxidation

A comparison of the adipic acid degradation (loss) data from four different test facilities was made. Most of the data also support these conclusions.

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1. INTRODUCTION

The use of buffering additives such as adipic acid in limestone flue gas desulfurization (FGD) wet scrubbers has been shown to benefit both SO_2 removal and limestone utilization. However, substantial loss of adipic acid was experienced during the long term scrubber tests. These losses were in excess of that expected from the scrubber solution discharged with the filter cake solids. Tests have also shown that the adipic acid loss rate is considerably higher during forced oxidation runs than during natural oxidation conditions. An increase of 80 percent in adipic acid consumption rate was observed in both EPA's test facilities at Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP) and at the TVA Shawnee Power Plant. The adipic acid loss was further verified by lab-scale experiments conducted by Radian Corporation.[1,2] Part of the observed loss was attributed to the oxidative degradation of adipic acid in the limestone FGD system.

In December 1979, a series of limestone-adipic acid factorial tests was conducted at the Shawnee test facility. Data from these tests indicated that the unaccountable adipic acid loss became negligible when the pH values were dropped below 5.[3] Furthermore, it was shown that no degradation loss was observed at pH below 5 even under forced oxidation conditions.[4] Since the quenching of the oxidative adipic acid degradation can substantially reduce the buffer additive consumption rate, the favorable operating conditions shown by the Shawnee results are very important to the application of adipic acid in full scale FGD systems. Acurex Corporation has been contracted by the EPA to conduct closed loop pilot plant scale SO_2 scrubber tests to study the effects of scrubber operating conditions on adipic acid degradation and other losses.

The specific objectives of the project are to:

- o verify the Shawnee results of zero adipic acid degradation under conditions of low pH
- o conduct studies to identify the effect of key operating variables on adipic acid degration and other losses.

During the period between 15 March and 30 September, 1980, Acurex conducted 12 adipic acid degradation tests. The operating variables whose effects were investigated during the reporting period include:

- o pH change from 5.6 to 4.6
- o sources of adipic acid
- o total sulfite level
- o forced oxidation at pH 4.6
- o fly ash effect
- o addition of metal ions (ferrous, ferric and manganous)

All the data and operating conditions are presented in a summarized form in this report. The detailed description of each test and material balance calculations can be found in monthly progress reports 42 through 47. (Chang, C.S., J.H. Dempsey, and R.H. Borgwardt, "Limestone Scrubbing of SO_2 at EPA/RTP Pilot Plant Monthly Progress Reports, April to September, 1980).

SECTION 2. ADIPIC ACID TESTING

Twelve tests were conducted at the EPA-IERL-RTP pilot scale limestone scrubber system. The scrubber is a three stage turbulent contact absorber (TCA) with 7.5 m^3/min flue gas capacity (0.1MW). No flyash was present in the flue gas which was drawn from a gas-fired boiler with the injection of pure SO_2. The oxygen content in the flue gas was controlled in the range of 5 to 6 percent. The limestone used for the tests was obtained from the EPA Shawnee Test Facility and is the same Fredonia White limestone used for TVA/Shawnee low pH adipic acid tests.

Two different scrubber configurations, natural and forced oxidation shown in Figures 2.1 and 2.2, were employed for the tests. The oxidizer consisted of a 30-cm diameter tower containing slurry at a depth of 5.5 m which was sparged with air at a stoichiometric ratio of 3.5 g-atom of oxygen per g-mole of SO_2 absorbed. A bleed stream of the slurry from the hold tank was directed to the clarifier and then processed by a rotary vacuum filter to remove the precipitated waste and all filtrate returned to the scrubber in a closed loop mode. All additives were fed to the hold tank. The pH in the hold tank was controlled by adjusting the limestone slurry feed rate.

Each run consisted of approximately 100 hours of continuous, steady-state operation. Eighteen slurry samples and six filter cake samples were taken during each run. A complete slurry analysis was made every eight hours and the results, averaged over the total run period, were used for the material balance.

Dry adipic acid powder was added to the hold tank at a constant rate every two hours. The adipic acid concentration in the scrubbing liquor was analyzed by ion chromotograph (IC) and checked by total carbon (TOC) analysis

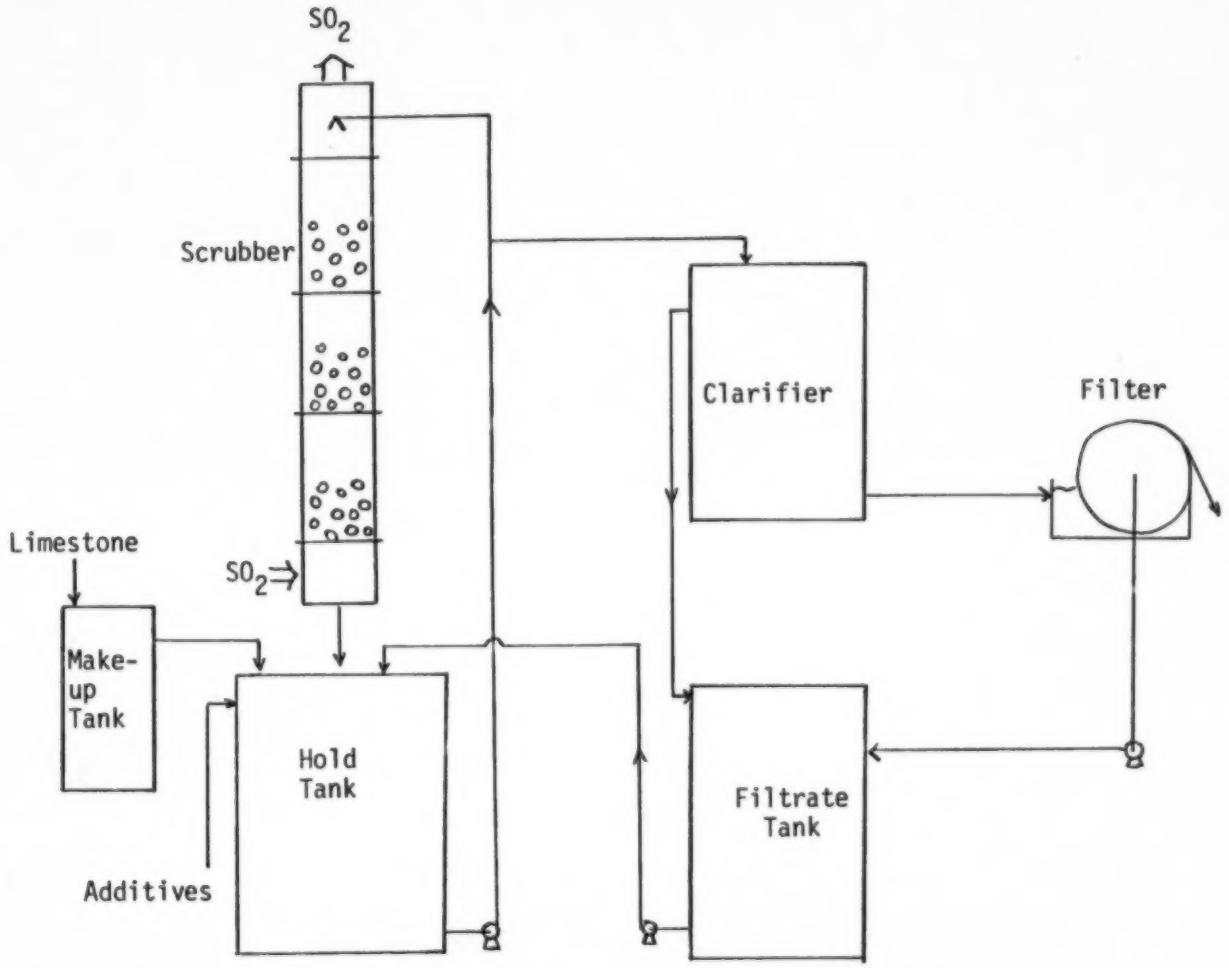

Figure 2.1. Flow diagram for single-loop natural oxidation tests in the limestone-TCA system.

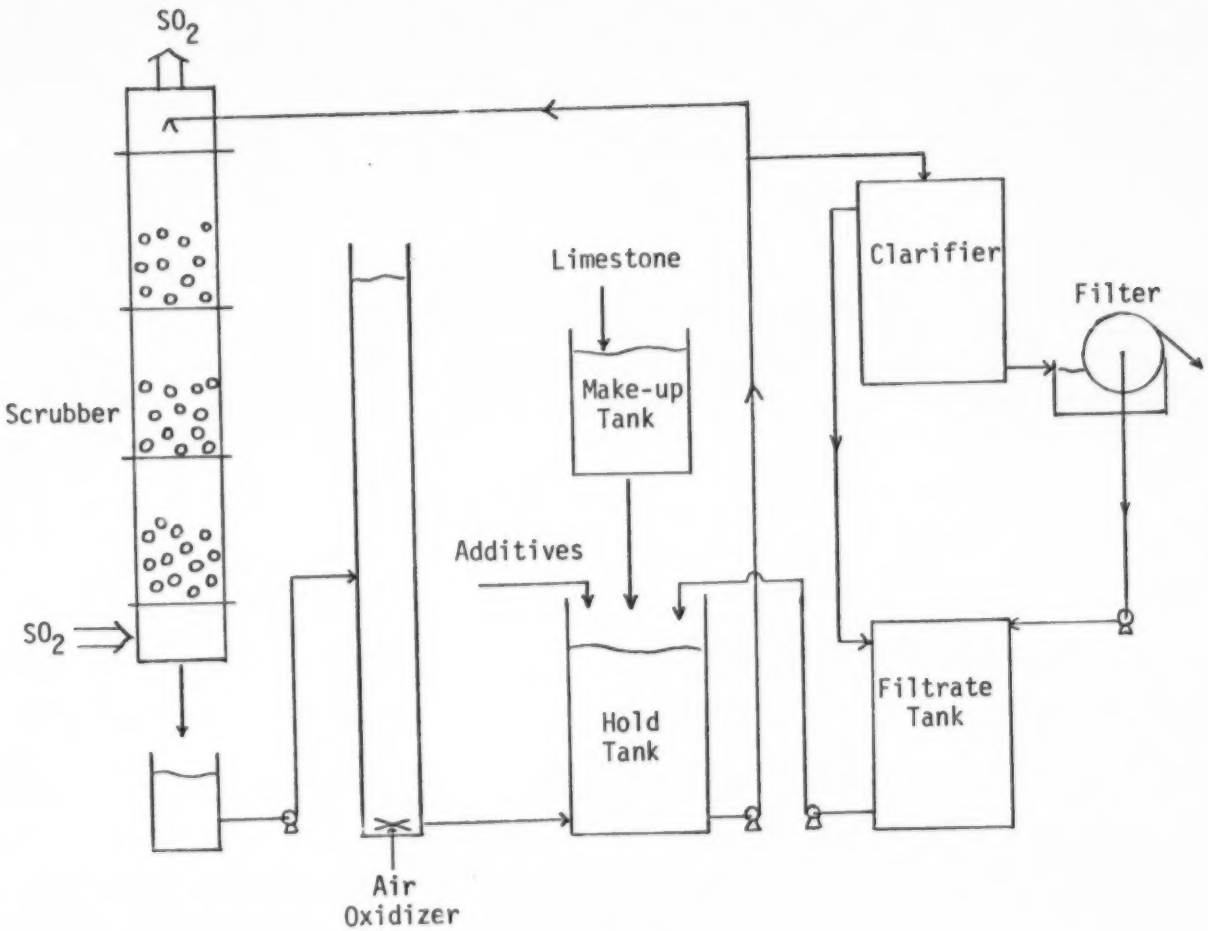

Figure 2.2. Flow diagram for the in-loop forced oxidation tests in the limestone-TCA system.

and silicic acid titration. A comparison of the results for standard adipic acid solutions is shown in Table 2.1. For the scrubber samples, TOC analysis and silicic acid titration usually give results slightly higher, less than 5 percent, than those by IC, as shown in Table 2.2. Sodium chloride was also added to the hold tank at a constant rate so that sodium could be used as a tracer to estimate the total liquor discharged. The total liquor discharged included liquid losses through the filter cake disposal, scrubber top carry-over, sampling, leaks at pipe fittings and pump seals, and other accidental losses. By using the sodium tracer, the adipic acid consumption from 'normal' scrubber solution losses could be accounted for. The adipic acid feed rate in excess of the accountable adipic acid loss was designated as unaccountable loss. Adipic acid degradation and coprecipitation with the scrubber solids were the two most likely causes of the unaccountable loss. It was the purpose of this project to investigate the changes in the unaccountable losses under various operating conditions, especially at pH values below 5.0.

Table 2.1

Comparison of Adipic Acid Standard Analyses (mg/l) by IC, TOC and Silic Acid Titration.

	known value	IC	TOC	Silicic Acid
#1	3150	3150	3139	3050
#2	1000	1020	1013	1066
#3	5480	5505	5542	5050
#4	1000	1015	1020	1034

Table 2.2

Comparison of Scrubber Sample Adipic Acid Analyses (mg/l) by IC, TOC and Silicic Acid Titration

Sample	IC	TOC	Silicic Acid
HTB, 4/22	4660	4770	4680
CBC, 4/24	3610	3750	3710
H-1	3120	3360	3310
H-2	3410	3470	3440
H-3	3080	3396	3310
H-4	3750	3790	3780

SECTION 3. RESULTS AND DISCUSSIONS

The major operating conditons and results of the twelve adipic acid tests are summarized in Table 3.1. The rationale and the unaccountable adipic acid loss of each test are listed in Table 3.2. Run H was the only forced oxidation test in the series, all others were with the single loop scrubber configuration shown in Figure 2.1.

Run A was designed to verify the Shawnee results of zero adipic acid loss at pH 4.6. It was also intended to compare the results with those at high pH under similar operating conditions. As is shown in Table 3.2 the unaccountable adipic acid loss of Run A at pH 4.6 is 5.7 g/hr or, 22 percent of the adipic acid feed, significantly different from the zero loss reported by Shawnee. The unaccountable loss under similar operating conditions but at pH 5.9 was 6 g/hr as previously reported.[5] Within the accuracy of the data, there was no significant difference between the unaccountable losses of adipic acid at pH 4.6 and 5.9 at the RTP pilot plant. The discrepancy between Shawnee's and RTP's low pH adipic acid degradation data indicate that there might be some factors other than pH which contribute to the quenching of degradation observed at Shawnee at low pH.

Since oxidative adipic acid degradation is very possibly a radical-induced chain reaction,[1] impurities introduced by the additives and reactants might act as an inhibitor and depress the degradation even when present in minute amounts. Industrial grade adipic acid manufactured by Celanese Corporation was used for Run A. For Run B, the same adipic acid used by Shawnee (Monsanto product) was added to the RTP limestone scrubber so that the effect of impurities from the two different sources of additives could be

Table 3.1

Major Operating Conditions: Limestone - TCA Scrubber Adipic Acid Tests

Run	A	B	C	D	E	F
Date	3/17-4/4	4/4-17	4/28-5/16	5/19-23	6/9-13	6/16-20
Liquid rate, gpm	26	26	16	16	20	20
Gas rate, cfm at 200° F	284	284	284	284	284	284
Inlet SO_2, ppm	2650	2650	2295	2295	2560	2560
SO_2 removal, %	73	72	87	88	85	87
Scrubber feed pH	4.6	4.55	4.59	4.61	4.56	4.61
Scrubber effluent pH	4.5	4.42	4.39	4.34	4.2	4.37
Oxidation, mole %	30	22	21	18	27	25
Limestone utilization, %	99	99	99	99	99	99
Fly ash, % of solids	0	0	0	0	30	0
Fe feed rate, g/hr	0	0	0.55	0	0	0
Mn feed rate, g/hr	0	0	0	0	0	0
Na feed rate, g/hr	47.2	47.2	25.9	25.9	23.6	23.6
Adipic Acid feed rate, g/hr	26	26	24	24	20	20
Total sulfite, g/hr	5.8	6.54	1.89	1.29	2.35	1.93
Na , g/hr	7.57	7.31	4.5	4.32	3.25	3.25
Adipic Acid , g/hr	3.67	3.62	3.27	3.15	2.13	2.08

Table 3.1 (Continued)

Major Operating Conditions: Limestone - TCA Scrubber Adipic Acid Tests

Run	G	H	I	J	K	L
Date	6/23-27	7/7-18	7/28-8/1	8/18-29	9/2-12	9/15-26
Liquid rate, gpm	20	20	20	20	20	20
Gas rate, cfm at 200° F	284	284	284	284	284	284
Inlet SO_2, ppm	2471	2560	2560	2560	2430	2430
SO_2 removal, %	85	68	81	96	82	83
Scrubber feed pH	4.58	4.5	4.63	5.7	4.63	4.52
Scrubber effluent pH	4.31	3.98	4.48	5.5	4.4	4.22
Oxidation, mole %	29	99	55	22	33	18
Limestone utilization, %	99	99	99	88	99	99
Flyash, % of solids	32	0	0	0	0	0
Fe feed rate, g/hr	0	0	0.68	0	0	1.3
Mn feed rate, g/hr	0	0	0.47	5.0	5.0	5.0
Na feed rate, g/hr	23.6	23.6	23.6	23.6	23.6	23.6
Adipic Acid feed rate, g/hr	20	20	20	20	20	20
Total sulfite, g/hr	3.1	0.45	3.62	1.35	4.13	3.08
Na , g/hr	2.97	2.63	3.69	3.59	3.45	2.35
Adipic Acid , g/hr	1.9	0.75	3.33	2.45	2.56	1.74

Table 3.2

Unaccountable Adipic Acid Losses
of Limestone - TCA Scrubber Tests

Run	Unaccountable Adipic Acid Loss g/hr	(% of total adipic acid feed)	Effects Investigated
A	5.7	(22)	low pH[a], moderate sulfite level
B	5.26	(20)	low pH; sources of adipic acid, moderate sulfite level
C	7.65	(32)	low pH, Fe^{2+}, low sulfite level[b]
D	8.0	(33)	low pH, low sulfite level
E	7.36	(37)	low pH, Duke flyash
F	7.66	(38)	replicate of D
G	7.57	(38)	low pH, Shawnee flyash
H	14.35	(72)	low pH, forced oxidation
I	2.6	(13)	low pH, Fe^{3+} and Mn^{2+}
J	7.43	(37)	high pH, Mn^{2+}
K	5.4	(27)	low pH, Mn^{2+}
L	5.4	(27)	low pH, Fe^{3+} and Mn^{2+} (replicate of I)

[a] low pH = 4.6 ±0.1

[b] All runs after B are with low sulfite level (adjusted by sodium feed rate)

observed. However, the results shown in Table 3.2 indicate that the origin of the adipic acid did not affect the rate of adipic acid loss significantly.

The total sulfite concentrations in Runs A and B were unusually high due to the low pH and high sodium feed rate. In order to lower the total sulfite concentration in the scrubbing liquor, the sodium feed rate was reduced from 47.2 to 27.54 g/hr and the total sulfite level decreased from about 6000 ppm to 2000 ppm. At the same time, ferrous chloride was added to the hold tank at a rate of 0.55 g/hr to test its effect on adipic acid degradation rate. Table 3.2 shows that 7.65 g/hr of unaccountable adipic acid was experienced with the addition of ferrous ion and the decrease in total sulfite concentration. Compared with the results of previous runs, the adipic acid loss increased by more than 30 percent in Run C. In order to identify the causes of this change on adipic acid loss, Run D was operated without the addition of ferrous chloride. No significant change in the rate of adipic acid loss was observed between Runs C and D. This indicates that the ferrous ions did not have a significant effect on degradation. The difference of adipic acid between Run C and Run B was attributed to the change of total sulfite concentration. In other words, high dissolved sulfite could reduce the rate of adipic acid loss. This was later confirmed by Rochelle et al[6] with lab-scale experiments. The probable reason for the observed results is that the excess sulfite ion acts as a scavenger for the free radicals which attack the adipic acid. As the total sulfite concentration increases, the number of free radicals available for adipic acid degradation should be decreased and thus decrease the adipic acid loss rate. However, the sulfite effect could not account for the discrepancy between Shawnee's and RTP's low pH degradation data. The sulfite level at Shawnee's scrubbing liquor was on the low side (less than 2,000 ppm) and there was still an appreciable amount of adipic acid loss at RTP although the total sulfite concentration was 6000 ppm.

One possible cause of the difference in adipic acid loss rates between RTP and Shawnee was the absence/presence of flyash. There was no flyash in RTP's simulated flue gas, but Shawnee was running with high fly ash loading. Some impurities might be introduced to the scrubbing slurry by flyash. The effect of flyash on adipic acid degradation rates was tested in Runs E, F and G. Flyash from Duke Power Company was added to the hold tank with limestone slurry at the rate of 4.4 lb/hr. The average flyash content of the solids in the scrubber system was about 30 percent. No flyash was added to the hold tank during Run F. All the other operating conditions remained the same as Runs E. For Run G, flyash from the Shawnee Power Plant was added to the hold tank with the limestone slurry at a rate of 4.8 lb/hr. The average flyash content of the solids in the scrubber system was about 32 percent. The material balance showed that the unaccountable adipic acid loss in the presence of flyash was about 7.5 g/hr (Table 3.2). Compared with the loss rate of 7.7 g/hr without flyash (Run F), no significant effect of flyash on adipic acid degradation rate was observed. For Runs E and G, the adipic acid concentration was analyzed by TOC (TC) analysis, silicic acid titration and IC, as in all other runs. Tables 3.3 and 3.4 show that the results from the former analyses were about 15 percent higher than those from the latter. Usually, the results from the former analyses were only about 5 percent higher than those from IC analysis without flyash. The relatively higher adipic acid concentration by TOC and silicic acid titration in the presence of flyash indicates that the flyash might contain a small amount of organic acid soluble in limestone slurries. If the silicic acid titration results were employed to make the material balance, the unaccountable adipic acid loss was reduced by 25 percent to about 5.7 g/hr which is still significantly higher than Shawnee's data of zero loss.

Table 3.3

Comparison of Adipic Acid Results (mg/l)
by IC, TOC and Silicic Acid Analyses with the
Addition of Flyash from Duke Power Company to H.T.

Sample	Date	IC	TOC	Silicic acid
CBA	6-3	2665	2903	2718
HTA	6-3	2120	2620	2336
HTC	6-3	2510	3017	3021
HTD	6-4	2765	3244	3242
HTE	6-4	2490	3040	2974
HTF	6-4	2490	2840	2700
CBG	6-5	2600	3000	2930
HTG	6-5	2700	3114	3045
CBI	6-5	2425	2636	2743
HTI	6-5	2425	2920	3035
Average		2499	2933	2874

Table 6.

Comparison of Adipic Acid Results (mg/l) by IC, TOC and Silicic Acid Analyses with the Addition of Shawnee Flyash to H.T.

Sample	Date	IC	TOC	Silicic Acid
HTC	6-24	2080	2140	1931
CBD	6-24	1996	2310	2248
HTD	6-24	1916	2170	2134
HTE	6-25	1940	2320	2311
HTF	6-25	1843	2310	2362
CBF	6-25	1743	2240	2232
HTH	6-26	1966	2300	2247
HTI	6-27	1896	2230	2231
Average		1923	2253	2212

Tests at Shawnee show that forced oxidation usually increases the adipic acid degradation rate when operating at pH greater than 5. Data from the Shawnee venturi-spray tests showed that adipic acid degradation could be quenched under either in-loop or bleedstream forced oxidation as long as the pH in the system was kept below 5 and limestone blinding did not occur. Run H at RTP was designed to verify the Shawnee results and to compare the adipic acid loss under forced oxidation at different pH values. The in-loop forced oxidation mode (Figure 2.2) was adopted for Run H. Material balance showed that the unaccountable loss of adipic acid was greatly increased (by 85 percent) with forced oxidation at pH 4.5. Similar increases of adipic acid loss were observed during high pH runs.[7] This shows that the adipic acid loss under forced oxidation is not significantly changed by pH.

The effect of manganous ion coupled with ferric and ferrous ions was tested with the lab-scale experiment at U.T. at Austin[6] while Run H was made at RTP. It was found that these metal ions may inhibit the adipic acid degradation to a great extent. In addition, the analysis of Shawnee scrubbing liquor showed that the manganese ion concentration could be as high as 50 ppm with forced oxidation.[8] It is possible that the manganous ion was partly responsible for the quenching of degradation at low pH at Shawnee. During Run I, manganous sulfate and ferric chloride were added to the hold tank at the rate of 1.28 g/hr and 2 g/hr, respectively. The steady state concentrations of Mn and Fe were only 17 and 12 ppm, respectively.* More than 95 percent of the metal ion added was lost, probably by coprecipitation with calcium sulfite. The material balance showed that the rate of unaccountable adipic acid loss was 2.6 g/hr in the presence of Mn and Fe ions. Compared with the loss rate of 7.7 g/hr under the same operating condition without Fe and Mn

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*The concentrations of Mn and Fe for all the previous runs were below 2 ppm.

addition, the adipic acid loss was reduced by 66 percent. The natural oxidation of Run H was 55 percent, considerably higher than the 25 percent (average) observed in previous runs. Also the higher natural oxidation was very close to the 50 percent obtained from Shawnee low pH adipic acid tests.[3] Therefore, it could be either the metal ions which quenched the degradation, or the high natural oxidation which affected the coprecipitation, or the compounded effects of both which resulted in the reduction of unaccountable adipic acid loss. If it were the metal ions, the manganous ion would be the most likely, because no effect of ferrous ion was found during Runs C and D. Since ferrous ion could be easily oxidized into ferric ion in the scrubber, it was reasonable to assume that ferric ion did not have an effect on degradation either.

Runs J and K were designed to test the effect of manganous ion on adipic acid degradation at both high and low pH values. Comparison of the results of Runs F and K (Table 3.2) shows that indeed manganous ion reduced the unaccountable adipic acid loss at low pH. Also, comparison of Runs J and K shows that the manganous ion was less effective in reducing the adipic acid loss at high pH value. However, the unaccountable adipic acid loss was neither zero (like Shawnee) nor as low as 2.6 g/hr (Run I).

Run L was intended to replicate Run I. Both ferric and manganous ions were added to the hold tank. The material balance showed that the unaccountable adipic acid loss was about 5.4 g/hr which is comparable to that of Run K but considerably higher than that of Run I. Comparison of the data shows that the natural oxidation of Run I (55 percent) was considerably higher than that of Runs K (33 percent) and L (18 percent). This led to the conclusion that manganous ion was only capable of reducing the unaccountable adipic acid loss from 7.7 g/hr to about 5.4 g/hr (compare Runs E, K and L).

The greater natural oxidation for Run I (55 percent) might be responsible for further decreasing the adipic acid loss from 5.5 g/hr to 2.6 g/hr (compare Runs I, K and L).

Unaccountable adipic acid loss was calculated as the total loss minus the losses through filter cake disposal, scrubber carry-over, sampling and accidental leaks. Therefore, unaccountable adipic acid loss consists of both the degradation and coprecipitation losses. It was important to identify each portion of the loss from total unaccountable adipic acid loss for further investigation and data interpretation. Several filter cake samples were sent to Radian Corporation for scrubber solids adipic acid analysis.[9] Those samples were reslurried in acetone and refiltered several times immediately after they were taken from the vacuum filter. It was believed that most of the entrained scrubbing liquor was diluted and washed away. The solid adipic acid contents of these samples are shown in Table 3.5. The data scattered from 510 to 2140 ug/gm. This indicates that some of the samples were not washed thoroughly. But even if we take the lowest number and assume that it represents the adipic acid coprecipitation loss, a significant portion of unaccountable adipic acid loss (about 40 percent) can still be attributed to coprecipitation. Therefore, the crystal structure and crystallization conditions (as well as oxidation conditions) might be important factors in reducing the adipic acid loss. Radian also reported that adipic acid coprecipitation was greatly reduced by oxidation.[9] This is in accordance with the observation at RTP (Runs I and L). Yet no evidence has shown that adipic acid coprecipitation can be reduced to zero at pH 4.6 with high natural oxidation.

Table 3.5.

Adipic Acid Contents in Filter Cake Solids from RTP Pilot Scrubber

Sample	Adipic Acid (Mg/gm)	Total Coprecipitation loss (g/hr) (TCL)	Unaccountable loss (g/hr) (UL)	Ratio TCL:UL
FC 4/3 (Run A)	535	2.3	5.7	0.4
FC 4/16 (Run B)	1260	5.27	5.26	1.0
FC 5/7 (Run C)	2140	10.7	7.65	1.4
FC 6/12 (Run E)	1090	5.1	7.36	0.69

SECTION 4. COMPARISON OF DATA

Data on adipic acid loss rates under limestone SO_2 scrubber conditions have been collected from four different facilities, Shawnee - 10 Mw pilot plant, RTP - 0.1 MW pilot plant, Radian - bench-scale, and U.T. at Austin - lab-scale experiments. Each facility has its own special features and reports the rate of loss differently. In order to make the data comparable, all data should be converted to the same units. The units adopted here, for natural oxidation condition, are mg unaccountable adipic acid loss per gm $CaSO_3 \cdot \frac{1}{2}H_2O$ formed for Shawnee's and RTP's data and mg adipic acid degradation per gm of $CaSO_3 \cdot \frac{1}{2}H_2O$ formed for Radian's data. The former results include both degradation and coprecipitation losses. Therefore, the actual degradation must be lower than the figures presented for Shawnee and RTP. Radian's data represents the actual degradation rate because the coprecipitation loss has been subtracted from the total loss. U.T. at Austin measured adipic acid degradation rate while oxidizing calcium sulfite slurry with pure oxygen. No calcium sulfite was formed and the experimental conditions were very close to those in the forced oxidation tank. Therefore, it is not feasible to compare the U.T. data with those obtained without forced oxidation. A comparison of the adipic acid degradation rates under natural oxidation condition is listed in Table 4.1. The quenching of adipic acid loss at pH below 5 at Shawnee is reflected by the zero loss rate shown in Table 4.1. For pH above 5.5, Shawnee's data scattered across one order of magnitude. Most high pH data are in the range of 1 to 2 mg unaccounted adipic acid per g of $CaSO_3 \cdot \frac{1}{2} H_2O$ formed. However, when Shawnee raised the pH from 4.6 to 5.5 incrementally from Run 921-1A to 1G, only 0.2 mg/g loss of adipic acid was observed.[3] Recent data of adipic acid loss in the TCA reached as high as 4.9 mg/g.[10] The RTP data

are all in a narrow range of 1 to 2 mg/g except Run I. The reason why the adipic acid loss at high pH is less than that at low pH is higher SO_2 removal was attained at higher pH and more $CaSO_3$ was formed. As discussed earlier, pH change did not affect the adipic acid loss per hour at RTP, the increase of $CaSO_3$ formed per hour resulted in a lower ratio of mg adipic acid loss per gm of $CaSO_3 \cdot \frac{1}{2}H_2O$ formed. Radian's data taken at Austin and Springfield showed an independent effect of pH on adipic acid degradation but data at Shawnee made this conclusion uncertain.[11] An examination of all the data indicates that

- The adipic acid degradation cannot be quenched only by decreasing the pH value below 5. Both RTP's and Radian's data support this inference. Shawnee's zero loss results require not only negligible degradation but also zero coprecipitation. There is no independent evidence to support either of these conditions.
- Some factors other than pH may affect the adipic acid degradation rate, especially at high pH. The scattered Shawnee data at pH above 5.5 support this inference. Some of Radian's data show a change of degradation with pH. But a careful comparison of all the data from Radian and RTP shows that degradation does not necessarily increase with pH. However, there may be some other factors which can result in high degradation at both low and high pH values.

The normalized adipic acid degradation rates under forced oxidation conditions from four different test facilities are listed in Table 4.2. The $CaSO_4 \cdot 2H_2O$ formed was used as the basis for comparison because gypsum dominated the solid phase for all runs. All the data except Shawnee's low pH and Radian's at Austin[11] are in the range of 2.5-4.9 mg/g.[12]

Table 4.1

Comparison of Normalized Adipic Acid Degradation (loss)
Rate Without Forced Oxidation

	mg, Adipic Acid Unaccounted / g, $CaSO_3 \cdot \frac{1}{2} H_2O$ Formed		mg, Adipic Acid Degraded / g, $CaSO_3 \cdot \frac{1}{2} H_2O$ Formed		
			Radian		
	Shawnee	RTP	Austin	Springfield	Shawnee
pH <5.0	0	1.66	1.5	0.9	5.1
pH >5.5	0.2-4.9	1.3	4.8	3.3	-

Table 4.2

Comparison of Normalized Adipic Acid Degradation (loss)
Rate With Forced Oxidation

	mg, Adipic Acid Unaccounted / g, $CaSO_4 \cdot 2H_2O$ Formed		mg, Adipic Acid Degraded / g, $CaSO_4 \cdot 2H_2O$ Formed	
	Shawnee	RTP	Radian	U.T. at Austin
pH <5.0	0	3.3	51	4.9
pH >5.5	4.2	2.5	47	-

The following points were made by the comparison of all the data.

- The adipic acid degradation rate does not become zero by only decreasing the pH below 5. Data from RTP, Radian and U.T. at Austin all show that an appreciable amount of adipic acid was degraded at pH below 5.
- Forced oxidation can increase the degradation even at pH below 5.
- RTP's and Radian's data show that pH change does not affect the adipic acid degradation rate. There may be some factors other than pH which caused Radian's data to be one order of magnitude higher than the rest.

SECTION 5. REFERENCES

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